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(54) 【発明の名称】 負極表面に混合導電性を付与した固体電解質

## (57) 【要約】

【目的】 高温固体電解質型水蒸気電解装置または高温固体電解質型燃料装置に使用される固体電解質に関する。

【構成】 高温固体電解質型水蒸気電解装置または高温固体電解質型燃料装置に用いる安定化ジルコニアを基体とする固体電解質において、下記群から選ばれた厚さ0.1～5 μmの混合導電性膜

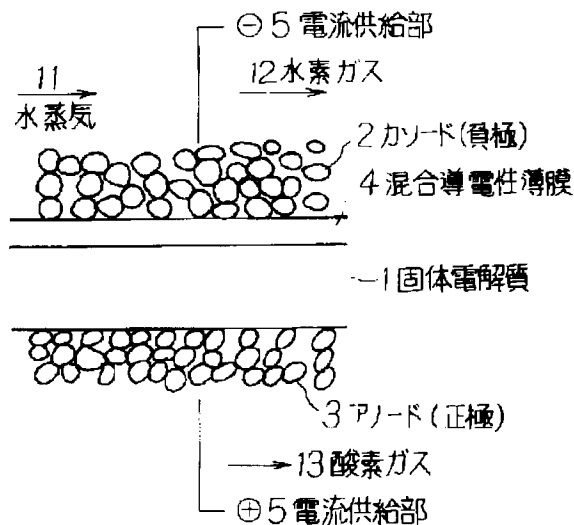
①  $La-Ce$  酸化物 (モル比率で  $La+Ce=1$  のとき、モル比で  $La:Ce=0\sim0.5:1.0\sim0.5$ )

②  $Y-Ce$  酸化物 (モル比率で  $Y+Ce=1$  のとき、モル比で  $Y:Ce=0\sim0.5:1.0\sim0.5$ )

③  $Pr$  酸化物

④  $Sm-Ce$  酸化物 (モル比率で  $Sm+Ce=1$  のとき、モル比で  $Sm:Ce=0\sim0.5:1.0\sim0.5$ )

を多孔質の負極表面に形成してなる負極表面に混合導電性を付与した固体電解質。



## 【特許請求の範囲】

【請求項1】 高温固体電解質型水蒸気電解装置または高温固体電解質型燃料装置に用いる安定化ジルコニアを基体とする固体電解質において、下記群から選ばれた厚さ0.1～5μmの混合導電性膜

① La-Ce酸化物（モル比率でLa+Ce=1のとき、モル比でLa:Ce=0～0.5:1.0～0.5）

② Y-Ce酸化物（モル比率でY+Ce=1のとき、モル比でY:Ce=0～0.5:1.0～0.5）

③ Pr酸化物

④ Sm-Ce酸化物（モル比率でSm+Ce=1のとき、モル比でSm:Ce=0～0.5:1.0～0.5）

を多孔質の負極表面に形成してなることを特徴とする負極表面に混合導電性を付与した固体電解質。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は高温固体電解質型水蒸気電解装置または高温固体電解質型燃料電池に使用される固体電解質に関する。

## 【0002】

【従来の技術】従来の高温固体電解質型水蒸気電解装置または燃料電池の構成を図4に示す。固体電解質1は平板であり、平板の固体電解質1の両側に負極2と正極3を設け、反応ガスの供給排出と電子の授受を担わせている。なお、図中、5は電流供給部（高温水蒸気電解装置の場合）を示す。負極2としては、一般にはNiと固体電解質の構成材料であるイットリア安定化ジルコニアのサーメットが使われ、正極3としては、一般にはLaMnO<sub>3</sub>等のペロブスカイト化合物が用いられる。

【0003】これらの電極では燃料電池と水蒸気電解装置では逆の反応が起こるため、各々について説明する。高温水蒸気電解操作においては次の反応がおこる。負極2では水蒸気11が供給され、負極2と固体電解質1の界面部では、負極2から電子が供給され、水蒸気11が分解されて水素ガス12が生成する。また、正極3では固体電解質1中移動した酸素イオンが電子を放出し、酸素ガス13が生成する。燃料電池操作においては次の反応がおこる。正極3では酸素が電子を受領して酸素イオンとなり、固体電解質1中を負極2に向けて移動する。負極2では酸素イオンは電子を放出して供給された水素11と反応して水蒸気12を生成する。

## 【0004】

【発明が解決しようとする課題】従来の方法の場合の問題点を以下に述べる。前項で説明した作動原理に基づいて燃料電池および高温水蒸気電解操作が行われるが、負極2での反応が起こる場所は固体電解質1と負極2および原料ガス（電解の場合は水蒸気、電池の場合は水素ガス）11が接するところ（これを三相界面と呼ぶ）に限

定される。なぜなら、電子の供給／放出、原料の供給、酸素イオンの固体電解質中への出入りの3つの要素のいずれかが欠けても反応が成立しないからである。高温水蒸気電解装置の負極2付近でおこる現象の模式図を図5に示す。

【0005】原料ガスの供給（燃料電池の場合は水素、高温水蒸気電解の場合は水蒸気）11および生成ガス（燃料電池の場合は水蒸気、高温水蒸気電解の場合は水素）12の排出のためには電極は多孔質である必要があり、そのため、図4に示すように電極は数～10μmの比較的大きな粒子が用いられてきた。

【0006】この場合、実際に反応が起こる面積が小さいことが欠点である。たとえ原料ガスがその場所では十分に分解されていても、有効面積は上述した3相界面に限定されるため、固体電解質の面積あたりに換算すると、実際の反応面積は小さくなってしまふ欠点があった。本発明はこのような課題をかんがみて、有効反応面積が大きい高性能の反応能力を発揮する固体電解質の構成を提供するものである。

## 【0007】

【課題を解決するための手段】本発明は高温固体電解質型水蒸気電解装置または高温固体電解質型燃料装置に用いる安定化ジルコニアを基体とする固体電解質において、下記群から選ばれた厚さ0.1～5μmの混合導電性膜

① La-Ce酸化物（モル比率でLa+Ce=1のとき、モル比でLa:Ce=0～0.5:1.0～0.5）

② Y-Ce酸化物（モル比率でY+Ce=1のとき、モル比でY:Ce=0～0.5:1.0～0.5）

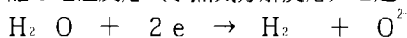
③ Pr酸化物

④ Sm-Ce酸化物（モル比率でSm+Ce=1のとき、モル比でSm:Ce=0～0.5:1.0～0.5）

を多孔質の負極表面に形成してなることを特徴とする負極表面に混合導電性を付与した固体電解質である。

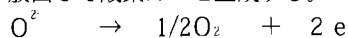
## 【0008】

【作用】本発明による固体電解質の作用を水蒸気電解の場合を例にとって以下図1及び図2によって説明するが燃料電池の場合も移動方向が逆となるだけで基本的には同じ作用となる。図1は本発明の固体電解質の構成の説明図、図2はその作用の説明図である。固体電解質1の負極2側表面に形成された電子導電性及びイオン導電性を合わせもつ混合導電性薄膜4は、固体電解質である安定化ジルコニア（以下、YSZと略す）1との界面で下記の電極反応（水蒸気分解反応）を起こす。



ここで、H<sub>2</sub>O（水蒸気）11は多孔質の負極2と混合導電性薄膜4中を拡散してYSZよりなる固体電解質1表面に到達する。また、電子eは電子導電性をもつ負極

2から混合導電性薄膜4を経て固体電解質1表面に供給され、電子を得た酸素イオン $O^{2-}$ は固体電解質1中を移動して正極3に向かう。正極3では酸素イオンは電子を放出して酸素ガスを生成する。



【0009】このように、本発明における作用の特徴として水蒸気分解反応が固体電解質1の全表面にわたって起こる点にある。その理由は混合導電性薄膜4が電子もガスも酸素イオンも通すことができるためである。

【0010】以上、水蒸気電解の場合を述べたが、燃料電池の場合には逆であり、正極3から負極2に酸素イオンが移動し、負極では混合導電性薄膜4のいたる所で水素と反応し、水蒸気を生成する。

【0011】なお、固体電解質本来の機能としては輸率 $\gamma$ が望ましく、その観点からは混合導電性薄膜は薄いほど好ましいが、薄すぎると有効電極面積を広げるといふ本発明の作用・効果が発現しなくなるので、その厚さは0.1~5 $\mu m$ にするのがよい。

【0012】

【実施例】本発明による実施例を前述した図1及び図2に基づいて説明する。固体電解質1は8mol%のイットリウムで安定化したジルコニア(YSZ)であり、0.5 $\mu m$ の粒子にアルコールと界面活性剤を加えてスラリー化し、テフロンシート上にこのスラリーを載せて自然乾燥させた後、1500℃で1時間、空气中で焼成して得た。生成したYSZ板は75mm×75mmの平板であり、厚さは250 $\mu m$ である。このジルコニア基板を以下の実施例で用いた。

【0013】(実施例1)  $La(NO_3)_3 \cdot 6H_2O$ と $Ce(NO_3)_3 \cdot 6H_2O$ を重量比1対3で混合(La対Ceのモル比0.25:0.75)し、これに水を重量比30%加えて溶液とする。これを上述のYSZ板1の一面に塗布して1400℃で10時間焼成し、0.5~1.0 $\mu m$ 厚の混合導電性薄膜4を形成させた。(この厚さはEPMa検出限界以下であるが、蛍光X線で存在することが確認される範囲のものである)この薄膜4上に負極2としてNiO:60重量%とYSZ:40重量%を混合したスラリーを常法のスクリーン印刷法により施工した。また正極3としては $LaMnO_3$ を同じ方法で施工した。これを1300℃で焼成してセルを製造した。LaとCeのモル比についてはLaのモル比を0.5以上とすると混合導電性が弱くなり目的とする効果を発揮できない。

【0014】(実施例2)  $Ce(NO_3)_3 \cdot 6H_2O$ と $Y(NO_3)_3 \cdot 6H_2O$ を重量比2.36対1で混合(Ce対Yのモル比0.6:0.4)とし、これに水を加えて飽和溶液としたものをYSZ板1に塗布し、大気中で1400℃で10時間焼成し、0.5~1.0 $\mu m$ 厚の混合導電性薄膜4を形成させた。以下の工程は実施例1と同じである。

【0015】(実施例3)  $Sm(NO_3)_3 \cdot 6H_2O$ と $Ce(NO_3)_3 \cdot 6H_2O$ を重量比1対3.9で混合(Sm対Ceのモル比0.20:0.80)し、これに水を重量比40%加えて溶液とする。これを上述のYSZ板1の一面に塗布して1400℃で10時間焼成し、0.5~1.0 $\mu m$ 厚の混合導電性薄膜4を形成させた。以下の工程は実施例1と同じである。

【0016】(実施例4) 硝酸セリア $Ce(NO_3)_3 \cdot 6H_2O$ を水に溶解し、50重量%の溶液とした。この液をYSZ板1に塗布し、大気中で1400℃で10時間焼成し、0.5~1.0 $\mu m$ 厚の混合導電性薄膜4を製造した。以下の工程は実施例1と同じである。

【0017】(実施例5) 硝酸プラセオジウム $Pr(NO_3)_3$ 液をYSZ板1に塗布し、大気中で焼成して0.5~1.0 $\mu m$ 厚の混合導電性薄膜4を製造した。X線回折によって $Pr_2O_3$ を確認した。以下の工程は実施例1と同じである。

【0018】以上の実施例1~5で製造したセルを用い、温度1000℃で水蒸気を供給して水蒸気電解を行った場合の電位-電流曲線を図3に示す。ここで、電流密度(横軸)を増加すると負極電位(縦軸)は性能の悪いセル程負に大きくなる傾向を示す。黒丸で示した従来セルに比べて、実施例1~5のセルではいずれも電位の変化は小さく、一定の電流密度を得るための電位は小さくて済むことを示している。

【0019】また、固体電解質の耐久性が向上する。固体電解質に加わる電位が卑になると、具体的には空気を参照極とする電位がおよそ-1.4V以下になるとYSZが還元される等によって劣化する現象がおこる。本発明においては、反応が固体電解質の全表面で起こるため、局部的に電流が集中しない。そのため、電位が従来法に比べて貴に保つことができ、これは固体電解質の耐久性の向上に寄与する。

【0020】電流密度600mA/cm<sup>2</sup>で定電流電解を行った場合、従来例では24時間以内にセルが劣化して抵抗が大きくなり通電不能となったが、上記実施例では安定した通電が100時間以上可能であった。

【0021】

【発明の効果】本発明の負極表面に混合導電性付与した固体電解質を使用することにより、高温水蒸気電解装置、高温固体電解質型燃料装置の電解セルは性能が向上し、固体電解質自体の耐久性も向上する。

【図面の簡単な説明】

【図1】本発明の一実施例の固体電解質型高温水蒸気電解装置の説明図。

【図2】本発明の固体電解質型高温水蒸気電解装置の負極付近でおこる現象の説明図。

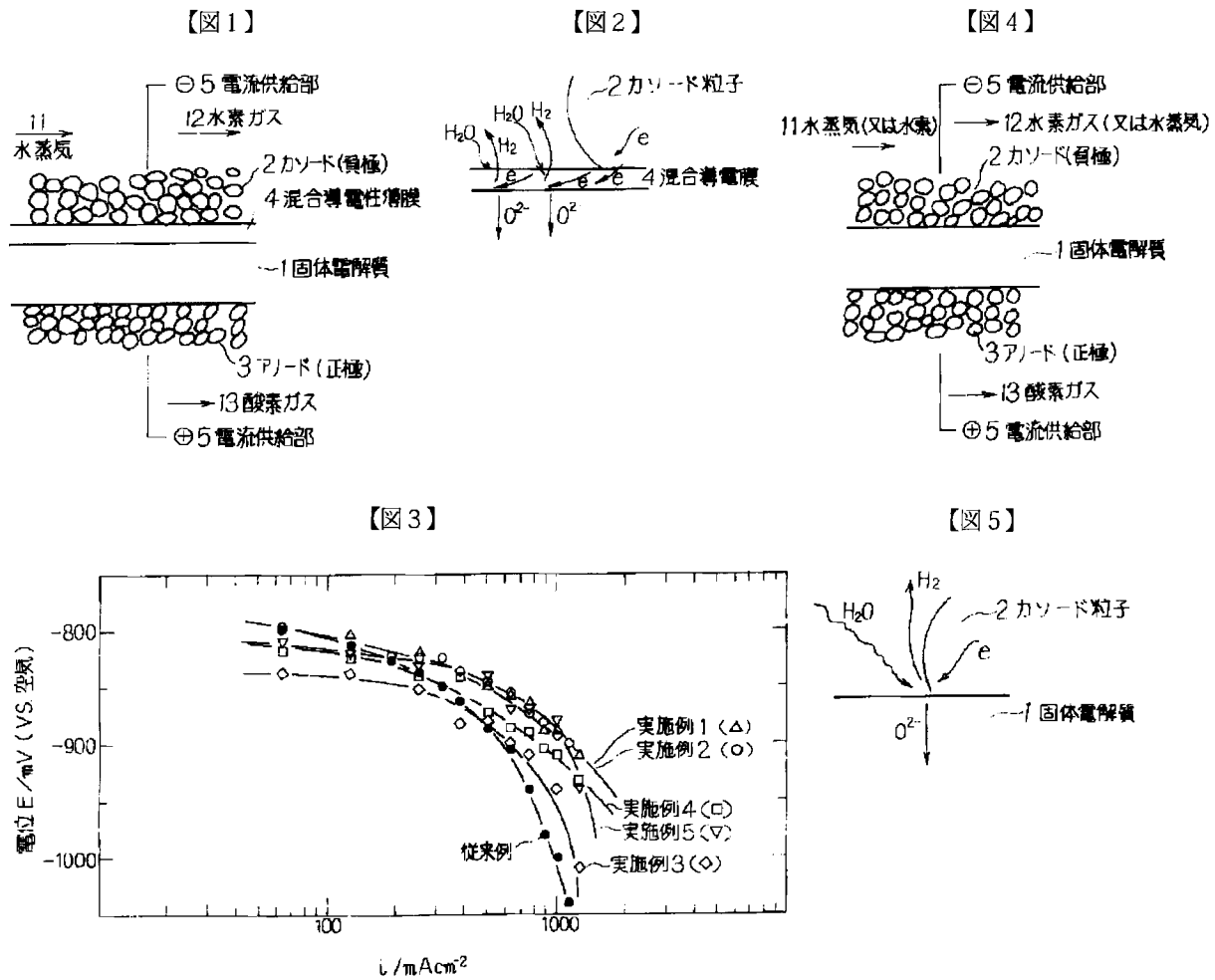
【図3】本発明の固体電解質と従来の固体電解質を用いた高温水蒸気電解装置の性能の比較図表。

【図4】従来の固体電解質型高温水蒸気電解装置の原理

の説明図。

\* 付近でおこる現象の説明図。

【図5】従来の固体電解質型高温水蒸気電解装置の負極\*



フロントページの続き

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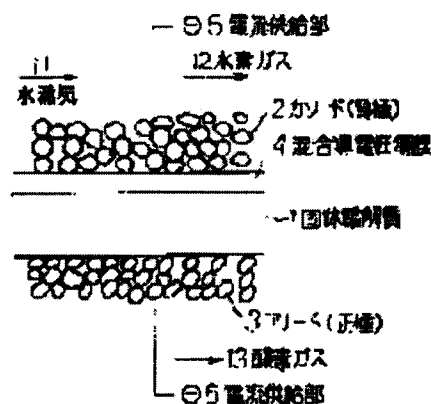
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(54) SOLID ELECTROLYTE WITH MIXED CONDUCTIVITY GIVEN TO SURFACE OF NAGATIVE ELECTRODE

(57)Abstract:

PURPOSE: To improve the performance of the electrolytic cells of a high temperature electrolysis device and a high temperature solid electrolytic fuel device, and to improve the durability of a solid electrolyte itself by using electrolyte for which mixed conductivity is given to the surface of a negative electrode.

CONSTITUTION: A solid electrolyte 1 is YSZ, and a surface active agent is added to a particle of 0.5 $\mu$ m to form a slurry, which is placed on a Teflon sheet, and after the slurry is dried naturally, it is backed in the atmosphere. Materials La (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O are mixed together at the weight ratio of 1 to 3, to which water is added by 30% by weight ratio and a solution is provided. This solution is applied to one surface of the VSZ plate 1 and is baked to form a mixed conductivity thin film 4. A slurry for which 60wt.% of NiO and 40wt.% of YSZ are mixed together is screen-printed as a negative electrode on the thin film 4. A material LaMnO<sub>3</sub> is provided in the same manner to provide a positive electrode. This electrode is baked to form a cell.



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3.In the drawings, any words are not translated.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the solid electrolyte used for an elevated-temperature solid oxide type water-vapor-electrolysis device or an elevated-temperature solid oxide fuel cell.

[0002]

[Description of the Prior Art]The composition of the conventional elevated-temperature solid oxide type water-vapor-electrolysis device or a fuel cell is shown in drawing 4. The solid electrolyte 1 is monotonous, forms the negative electrode 2 and the anode 3 in the both sides of the monotonous solid electrolyte 1, and is making supply discharge of reactant gas, and electronic transfer bear. Five show a current supply source part (in the case of a high-temperature-steam electrolytic device) among a figure. As the negative electrode 2, the cermet of the yttria stabilized zirconia which is generally a component of nickel and a solid electrolyte is used, and, generally perovskite compounds, such as  $\text{LaMnO}_3$ , are used as the anode 3.

[0003]By these electrodes, with a fuel cell and a water-vapor-electrolysis device, since a reverse reaction occurs, each is explained. The next reaction starts in high-temperature-steam electrolysis operation. In the negative electrode 2, the steam 11 is supplied, in the interface part of the negative electrode 2 and the solid electrolyte 1, an electron is supplied from the negative electrode 2, the steam 11 is disassembled, and the hydrogen gas 12 generates. In the anode 3, the oxygen ion which moved among the solid electrolyte 1 emits electrons, and the oxygen gas 13 generates. The next reaction starts in fuel cell operation. In the anode 3, an electron is received and it becomes oxygen ion, and oxygen turns the inside of the solid electrolyte 1 to the negative electrode 2, and moves. In the negative electrode 2, oxygen ion reacts to the hydrogen 11 supplied by emitting electrons, and generates the steam 12.

[0004]

[Problem(s) to be Solved by the Invention]The problem in the case of the conventional method is described below. Although a fuel cell and high-temperature-steam electrolysis operation are performed based on the working principle explained for the preceding clause, the place where the reaction in the negative electrode 2 occurs is limited to the place (this is called a three-phase zone) where the solid electrolyte 1, the negative electrode 2, and the material gas (it is the steam and hydrogen gas in the case of a cell in the case of electrolysis) 11 touch. It is because a reaction is not materialized even if either of three elements of receipts and payments into electronic supply/discharge, supply of a raw material, and the solid electrolyte of oxygen ion is missing. The mimetic diagram of the phenomenon started near [ negative-electrode 2 ] a high-temperature-steam electrolytic device is shown in drawing 5.

[0005]the electrode being porosity, therefore for the supply (it is hydrogen and the steam in the case of high-temperature-steam electrolysis in the case of a fuel cell) 11 of material gas, and discharge of the production gas (it is the steam and hydrogen in the case of high-temperature-steam electrolysis in the case of a fuel cell) 12, As shown in drawing 4, as for the electrode, the number -10micrometer comparatively big particle has been used.

[0006]In this case, it is a fault that the area in which a reaction actually occurs is small. Since a usable area would be limited to the three-phase-circuit interface mentioned above even if material

gas is fully decomposed at the place, when it converted per area of a solid electrolyte, the actual reaction surface product had a fault which becomes small. This invention provides the composition of the solid electrolyte in which an effective reaction surface product demonstrates highly efficient large competence power in view of such a technical problem.

[0007]

[Means for Solving the Problem] In a solid electrolyte in which this invention uses as a base stabilized zirconia used for an elevated-temperature solid oxide type water-vapor-electrolysis device or an elevated-temperature solid oxide type fuel system, A 0.1-5-micrometer-thick mixed conductive film \*\* La-Ce oxide chosen from the following group (it is a mole ratio in mole fraction at the time of La+Ce=1, and is La:Ce=0-0.5:1.0-0.5)

\*\* Y-Ce oxide (it is a mole ratio in mole fraction at the time of Y+Ce=1, and is Y:Ce=0-0.5:1.0-0.5)

\*\* Pr oxide \*\* Sm-Ce oxide (it is a mole ratio in mole fraction at the time of Sm+Ce=1, and is Sm:Ce=0-0.5:1.0-0.5)

It is the solid electrolyte which gave mixed conductivity to a negative electrode surface which forms in a porous negative electrode surface and is characterized by things.

[0008]

[Function] Although drawing 1 and drawing 2 explain an operation of the solid electrolyte by this invention below taking the case of the case of water vapor electrolysis, also when it is a fuel cell, it becomes the same operation fundamentally only by the move direction becoming reverse. Drawing 1 is an explanatory view of the composition of the solid electrolyte of this invention, and drawing 2 is an explanatory view of the operation. The mixed conductive thin film 4 which doubles and has the electron conductivity and ion conductivity which were formed in negative-electrode 2 side surface of the solid electrolyte 1 causes the following electrode reaction (steam-cracking reaction) by an interface with the stabilized zirconia (it abbreviates to YSZ hereafter) 1 which is a solid electrolyte.  $\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2$  O(steam) 11 arrives at the solid electrolyte 1 surface which diffuses the inside of the porous negative electrode 2 and the mixed conductive thin film 4, and consists of YSZ(s) +  $\text{O}^{2-}$   $\text{H}_2$  here. The solid electrolyte 1 surface is supplied through the mixed conductive thin film 4 from the negative electrode 2 with electron conductivity, oxygen ion  $\text{O}^{2-}$  which obtained the electron moves in the inside of the solid electrolyte 1, and the electron e faces to the anode 3. In the anode 3, oxygen ion emits electrons and generates oxygen gas.

$\text{O}^{2-} \rightarrow 1/2\text{O}_2 + 2\text{e}^-$  [0009] Thus, it is in the point which a steam-cracking reaction starts over all the surfaces of the solid electrolyte 1 as a feature of the operation in this invention. The reason is because the mixed conductive thin film 4 can let an electron, gas, and oxygen ion pass.

[0010] As mentioned above, although the case of water vapor electrolysis was described, in the case of a fuel cell, it is reverse, and oxygen ion moves to the negative electrode 2 from the anode 3, in a negative electrode, it reacts to hydrogen everywhere in the mixed conductive thin film 4, and a steam is generated.

[0011] As an original function of a solid electrolyte, transference number =1 is desirable, and although the mixing conductive thin film from the viewpoint is so preferred that it is thin, since an operation and effect of this invention of extending effective electrode area stop being revealed when too thin, it is good [ the thickness ] to use 0.1-5 micrometers.

[0012]

[Example] It explains based on drawing 1 and drawing 2 which mentioned the example by this invention above. It was the zirconia (YSZ) stable by 8-mol% of yttria, the solid electrolyte 1 added and slurred alcohol and a surface-active agent to a 0.5-micrometer particle, and after carrying and carrying out natural seasoning of this slurry on a Teflon sheet, it obtained them by calcinating it in the air at 1500 \*\* for 1 hour. The generated YSZ board is a plate (75 mm x 75 mm), and thickness is 250 micrometers. This zirconia board was used in the following examples.

[0013] (Example 1)  $\text{La}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$ , and  $\text{Ce}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$  are mixed by three in one pair of weight ratio (mole ratio 0.25:0.75 of La pair Ce), 30% of a weight ratio adds water to this, and it is considered as a solution. This was applied to the whole surface of the above-mentioned YSZ board 1, it calcinated at 1400 \*\* for 10 hours, and the mixed conductive thin film 4 of 0.5-1.0-micrometer thickness was made to form. (Although this thickness is below an EPMA detection limit, it is a thing

of the range by which existing with fluorescence X rays is checked)

The slurry which mixed NiO:60 % of the weight and YSZ:40 % of the weight as the negative electrode 2 on this thin film 4 was constructed with the screen printing of the conventional method. As the anode 3,  $\text{LaMnO}_3$  was constructed by the same method. This was calcinated at 1300 °C and the cell was manufactured. If the mole ratio of La is made or more into 0.5 about the mole ratio of La and Ce, mixed conductivity becomes weak and the target effect cannot be demonstrated.

[0014](Example 2)  $\text{Ce}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$ , and  $\text{Y}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$  are considered as mixing (mole ratio 0.6:0.4 of the Ce pair Y) by the weight ratio 2.36 to 1, What added water to this and was used as the saturated solution was applied to the YSZ board 1, it calcinated at 1400 °C in the atmosphere for 10 hours, and the mixed conductive thin film 4 of 0.5–1.0-micrometer thickness was made to form. The following processes are the same as Example 1.

[0015](Example 3)  $\text{Sm}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$ , and  $\text{Ce}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$  are mixed by the weight ratio 1 to 3.9 (mole ratio 0.20:0.80 of Sm pair Ce), 40% of a weight ratio adds water to this, and it is considered as a solution. This was applied to the whole surface of the above-mentioned YSZ board 1, it calcinated at 1400 °C for 10 hours, and the mixed conductive thin film 4 of 0.5–1.0-micrometer thickness was made to form. The following processes are the same as Example 1.

[0016](Example 4) Nitric acid Seria  $\text{Ce}(\text{NO}_3)_3$  and  $6\text{H}_2\text{O}$  were dissolved in water, and it was considered as 50% of the weight of the solution. This liquid was applied to the YSZ board 1, it calcinated at 1400 °C in the atmosphere for 10 hours, and the mixed conductive thin film 4 of 0.5–1.0-micrometer thickness was manufactured. The following processes are the same as Example 1.

[0017](Example 5) Nitric acid praseodymium  $\text{Pr}(\text{NO}_3)_3$  liquid was applied to the YSZ board 1, it calcinated in the atmosphere, and the mixed conductive thin film 4 of 0.5–1.0-micrometer thickness was manufactured.  $\text{Pr}_6\text{O}_{11}$  was checked according to the X diffraction. The following processes are the same as Example 1.

[0018]The potential-current curve at the time of supplying a steam at the temperature of 1000 °C and performing water vapor electrolysis using the cell manufactured in above Examples 1–5, is shown in drawing 3. Here, when current density (horizontal axis) is increased, negative-electrode potential (vertical axis) shows the tendency to become large negative as a powerless cell. Compared with the cell, each shows that change of potential is small, the potential for obtaining fixed current density is small, and it ends in the cell of Examples 1–5 conventionally which was shown by the black dot.

[0019]The endurance of a solid electrolyte improves. If the potential which will specifically make air a reference pole if the potential added to a solid electrolyte becomes °C becomes less than -1.4V about, the phenomenon that YSZ is returned etc. and in which it deteriorates will start. In this invention, since a reaction occurs on all the surfaces of a solid electrolyte, current does not concentrate locally. Therefore, potential can maintain at °C compared with a conventional method, and this contributes to improvement in the endurance of a solid electrolyte.

[0020]When electrolysis with constant current was performed by current density <sup>2</sup> of 600mA/cm, in the conventional example, the cell deteriorated within 24 hours, resistance became large, and energizing became impossible, but as for the energization stable in the above-mentioned example, 100 hours or more were possible.

[0021]

[Effect of the Invention]By using the solid electrolyte which carried out mixed addition of conductivity for the negative electrode surface of this invention, performance of the electrolysis cell of a high-temperature-steam electrolytic device and an elevated-temperature solid oxide type fuel system improves, and its endurance of the solid electrolyte itself also improves.

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[Translation done.]



\* NOTICES \*

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CLAIMS

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[Claim(s)]

[Claim 1]In a solid electrolyte which uses as a base stabilized zirconia used for an elevated-temperature solid oxide type water-vapor-electrolysis device or an elevated-temperature solid oxide type fuel system, A 0.1-5-micrometer-thick mixed conductive film \*\* La-Ce oxide chosen from the following group (it is a mole ratio in mole fraction at the time of La+Ce=1, and is La:Ce=0-0.5:1.0-0.5) \*\* A Y-Ce oxide (it is a mole ratio in mole fraction at the time of Y+Ce=1, and is Y:Ce=0-0.5:1.0-0.5) \*\* A Pr oxide \*\* Sm-Ce oxide (it is a mole ratio in mole fraction at the time of Sm+Ce=1, and is Sm:Ce=0-0.5:1.0-0.5)

A solid electrolyte which gave mixed conductivity to a negative electrode surface which forms in a porous negative electrode surface and is characterized by things.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1]The explanatory view of the solid oxide type high-temperature-steam electrolytic device of one example of this invention.

[Drawing 2]The explanatory view of the phenomenon started near the negative electrode of the solid oxide type high-temperature-steam electrolytic device of this invention.

[Drawing 3]The comparative diagram of the performance of the high-temperature-steam electrolytic device using the solid electrolyte of this invention, and the conventional solid electrolyte.

[Drawing 4]The explanatory view of the principle of the conventional solid oxide type high-temperature-steam electrolytic device.

[Drawing 5]The explanatory view of the phenomenon started near the negative electrode of the conventional solid oxide type high-temperature-steam electrolytic device.

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[Translation done.]

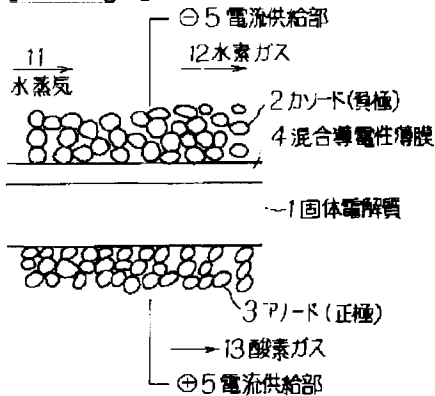
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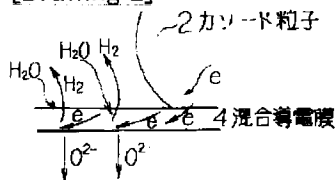
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## DRAWINGS

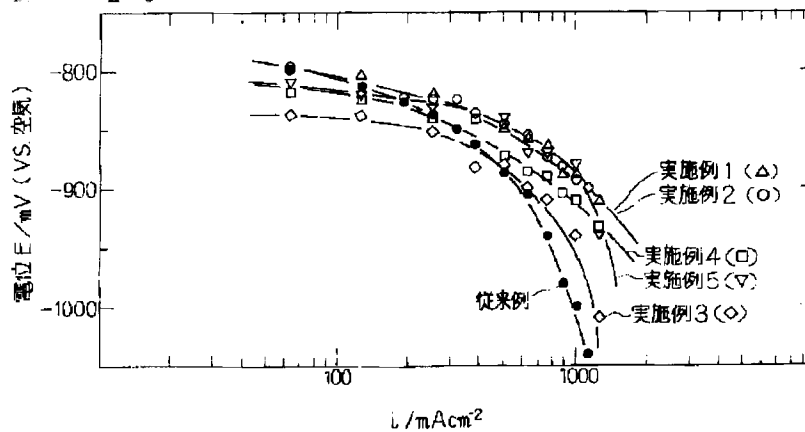
[Drawing 1]



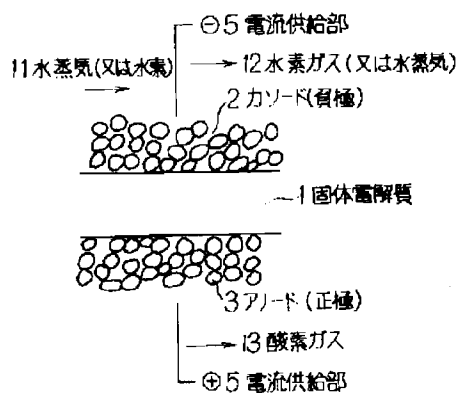
[Drawing 2]



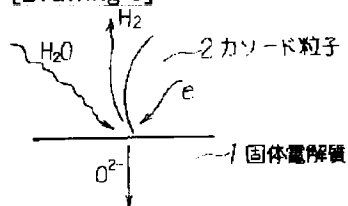
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]